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STUDIES OF THE AUGMENTATION OF REACTION RATES VIA LASER IRRADIA--ETC(U)
OCT 76 S H BAUER, E R LORY, K CHIEN

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The objective of this research project, to discover a reaction, involving a sizable substrate (more than three atoms) the rate of which is selectively augmented by infrared laser radiation, has been achieved. A preliminary analysis led to criteria for the selection of an optimum reaction type, and for setting the most suitable experimental parameters. We selected to study the self-scavenging decomposition of a borane adduct: $2 H_3 BPF_3 \rightarrow B_2 H_6 + 2 PF_3$. The relative photolytic efficiencies of

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the various lines emitted by a CO_2 laser were measured as was also the dependence of the rate on laser power, gas pressure and reaction cell temperature. Specificity of vibrational excitation was demonstrated in several ways, most directly by the observed isotope fractionation of H/D and $^{10}B/^{11}B$ ratios. The mechanism of the photoactivation process which we developed is in quantitative agreement with the observed conversion. A dynamic model (based on a normal mode analysis) was proposed for the selective activation.

In a parallel study of borane adducts, we evaluated the thermodynamic and kinetic rate parameters for six exchange and abstraction reactions. Rational structures were proposed for the corresponding transition states.

FINAL TECHNICAL REPORT

During the grant period [09/1/73 - 08/31/76] our research efforts were devoted to the study of the mechanism of laser augmented reactions, utilizing a CO_2 cw electrical discharge laser. The rationale for the particular experimental configuration which we selected, and the choice of the test substances, was presented in the first paper of a series of four reports, two of which have been published and two are in process of publication. The most expeditious way to summarize the contents of these papers is to present their abstracts:

1. Infrared Laser Augmented Decomposition of H_3BPF_3,
   E. R. Lory, S. H. Bauer and T. Manuccia, J. Phys. Chem., _79_, 545 (1975).
   [Dr. Lory was supported as a Post Doctorate Research Associate]

Consideration of v-v and v-T relaxation rates for polyatomic molecules subsequent to their vibrational excitation by currently available laser fluxes led to a strategy for selecting reactants for which the possibility for successful augmentation of reaction by infrared irradiation is optimized. Several criteria are listed. While these are shown to be useful guides they do not constitute a sufficient set of conditions for predicting augmentation of reactions. The criteria were applied to the selection of reactants for a typical $2AB \rightarrow A_2 + 2B$ reaction, i.e., a self-scavenging system. The thermochemistry, essential vibrational spectroscopy, and kinetic parameters for the $H_3B \cdot PF_3$ decomposition are briefly summarized. The experimental arrangement is described and the results of a series of runs with a CO_2 laser (10.6 μ band) are presented. A number of tests were applied to demonstrate that the induced decomposition was indeed due to vibrational excitation and not to a net rise in temperature. No significant boron isotope effect was found.

A mechanism is proposed, based on the observed dependence of per cent decomposition on photon flux, and its specificity for the rotational line used for excitation. Use of a spectrophone greatly facilitated measurement of the optical absorption coefficients. It appears that the rate-determining step is $H_3B + H_3B \cdot PF_3^{(v \approx 3)} = B_2H_6 + PF_3$ with the vibrational excitation in specific modes.

2. Laser Augmented Decomposition II. D_3BPF_3

K-R. Chien and S. H. Bauer, J. Phys. Chem., <u>80</u>, 1405 (1976).
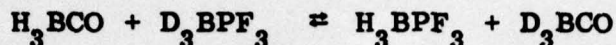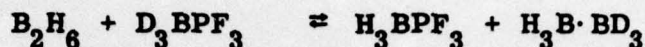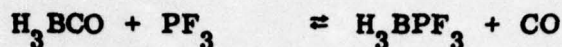
[Dr. Chien was supported as a Post Doctorate Research Associate.]

We continued the study of the accelerated decomposition of H_3BPF_3 induced by laser radiation (930-950 cm^{-1}), and extended it to the fully deuterated species. While in all essential respects the kinetics of their photolysis for the two compounds are identical, the few differences which were uncovered proved crucial in pointing to interesting features of the mechanism. These verified predictions based on a normal mode analysis for the distribution of potential energy among the internal coordinates. For the laser augmented decomposition, $E_a^L = 3.5 \pm 1$ kcal/mole, compared with $E_a^{th} = 29.3$ kcal/mole for the thermal process. The quantum efficiency is low, $\approx 4 \times 10^4$ photons/molecule decomposed. The rates of decomposition depend on the isotopic content and are sensitively dependent on the frequency of the irradiating line. For example, with P(24) large fractionation ratios were found for D_3BPF_3 <u>vs</u> H_3BPF_3, and small differences for $D_3{}^{11}BPF_3$ <u>vs</u> $D_3{}^{10}BPF_3$. The levels of decomposition induced by the sequential three-photon absorption have been semi-quantitatively accounted for.

3. Thermodynamic and Kinetic Parameters for Borane Exchanges,

K-R. Chien and S. H. Bauer, Accepted for publication in <u>J</u>. <u>Inorg</u>. <u>Chem</u>.

Equilibrium compositions and bimolecular exchange rates were measured at two temperatures, for the following reactions:

$$H_3BCO + PF_3 \rightleftharpoons H_3BPF_3 + CO$$

$$B_2H_6 + D_3BPF_3 \rightleftharpoons H_3BPF_3 + H_3B \cdot BD_3$$

$$H_3BCO + D_3BPF_3 \rightleftharpoons H_3BPF_3 + D_3BCO$$

These homogeneous reactions are of unit order in each of the reagents, with activation energies 13-15 kcal mole^{-1}. We included in this summary six analogous reactions for which rate data have been published, to demonstrate the existence of a consistent pattern for the borane exchange steps.

4. The Molecular Dynamics Problem in Multiphoton Excitation,
   S. H. Bauer and K-R. Chein, Accepted for publication in Chem. Phys. Lett.

While the molecular dyanmics for weakly coupled, harmonic oscillators under-going infinitesimal amplitude displacements are well described by normal modes, and the other extreme --- strongly coupled anharmonic, large amplitude oscillating units can be treated as though they are ergotic systems, so that only state densities are needed, intermediate cases are very difficult to analyze. Here we propose that some intermediate cases, wherein we seek relative rates for reaction induced by specific frequency excitation (three-center displacement reactions or dissociation), may be approximately estimated from a normal mode analysis by calculating increments in root mean square amplitudes for a suitable internal coordinate, upon specific multiple photon absorption. A test case is presented an an illustration.

No advanced degrees were awarded on the basis of work done on this project.